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Time-Resolved XAFS Studies of NiO Reduction Mechanism
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Beamline(s) X16C

Introduction: Using time-resolved (TR) XANES/EXAFS we monitored the structural changes and reaction kinetics during the reduction of NiO powders by hydrogen. The focus of these studies was to unveil the local scenario and kinetics of the reaction. One of the problems we intended to solve was: are there just the two end phases (rock-salt NiO and fcc Ni) heterogeneously mixed at any time during the reduction (Fig. 1)? Or the room is also left for a strongly disordered, and thus invisible for the XRD, short-living phase of an unknown nature (NiO_x)?

Experiment: All x-ray absorption data were measured in the transmission mode at three different reduction temperatures (260, 280 and 300°C). We prepared the samples from the NiO powder by spreading it over adhesive Kapton tape. After heating up, the samples were exposed to a flow of pure H_2 (~ 50 cm^3/min) while the XANES or EXAFS measurements were taken repetitiously (the repetition times were 4 and 20 min, respectively) during the reactions. Our experiments showed marked time-dependent effects in both the XANES (Fig. 2) and EXAFS (Fig. 3) data. To obtain the number and identities of the intermediate phases during the reaction, we used principal component analysis (PCA) of both XANES and EXAFS spectra. The number of principal components, sufficient to reproduce all the time-resolved spectra was found to be equal to 2 thus ruling out the presence of a disordered NiO_x phase at any time during the reduction. The time-dependent mixing fractions of NiO in all the samples and at all reduction temperatures were obtained (Fig. 4). These results clearly demonstrate the induction period required to generate O vacances in NiO while no intermediate NiO_x phase is formed.

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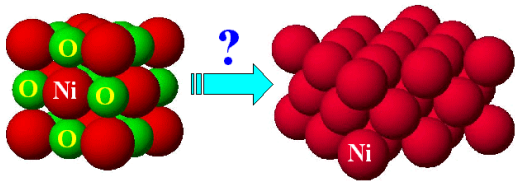

Figure 1. During the NiO → Ni lattice transformations, O vacances are formed in NiO lattice, but is any intermediate NiO_x phase formed along with Ni phase?

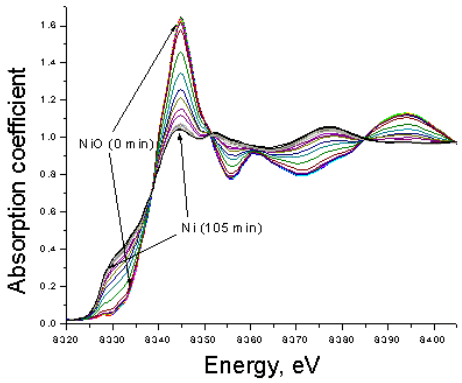

Figure 2. Time-resolved changes in normalized XANES data measured at 280°C

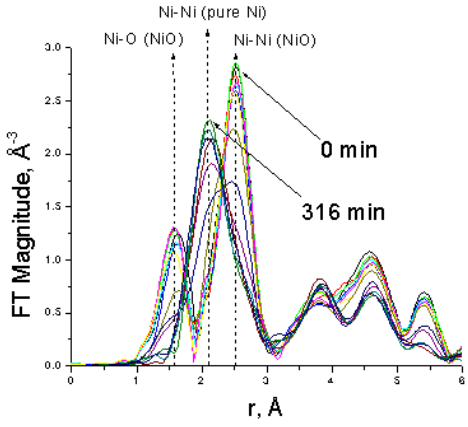

Figure 3. Time-resolved changes in Fourier-transformed k^2-weighted EXAFS data measured at 260°C

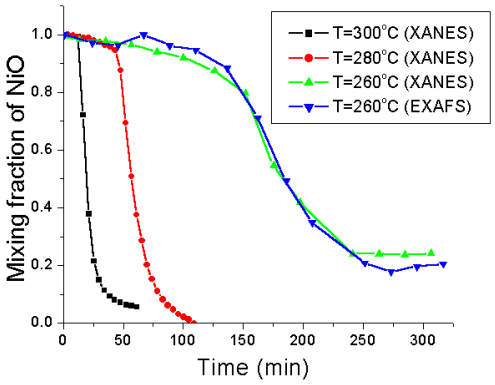

Figure 4. Mixing fraction of NiO as a function of time for reduction at different temperatures, as obtained from the XANES and EXAFS data by the PCA